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(54) Substantially solvent free organic material

(57) A substantially solvent-free composition comprises a base material dispersed within a liquid prepolymer system, the base material being selected from bitumen, asphalt, coal tar or a substantially non-volatile petroleum based material and the dispersion being stable at room temperature for at least about 30 days. The prepolymer may be an isocyanate prepolymer, e.g. a polyester or polyether polyurethane prepolymer, or a polyepoxide prepolymer. The composition preferably includes a compatibiliser having a non-polar component and a polar organic component, to disperse the base material into the liquid prepolymer. Suitable compatibilisers include propylene glycol monostearate, bis stearyl ester polypropylene diol, ethylene glycol monostearate, triethylene glycol caprate caprylate and triethylene glycol dipelargonate. The compositions can be used as coatings, adhesives and sealants.

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DESCRIPTION

"SUBSTANTIALLY SOLVENT FREE ORGANIC MATERIAL"

The present invention relates to curable, substantially solvent-free compositions particularly prepolymer curing systems in combination with asphalt based materials; bitumen based materials; coal tar; substantially non-volatile petroleum based materials, and the like. More specifically, the present invention is directed to the use of surfactant-type additives and derivatives thereof to disperse a base material into a liquid prepolymer system, thereby substantially eliminating the need for solvent in numerous coatings, adhesive, sealant and similar type applications.

Asphalt is a dark, cementitious material having a solid or semi-solid consistency. It occurs naturally or as a petroleum derivative and is generally composed primarily of bitumens, generally paraffinic and aromatic hydrocarbons and heterocyclic compounds containing sulphur, nitrogen, and oxygen.

Asphalt is relatively inexpensive and has a relatively high penetration value when applied to most porous surfaces. Furthermore, asphalt is relatively weather resistant and water impermeable. As a result,

asphalts have traditionally been used as protective films, adhesives, binders, and the like.

Asphalt can be used in a variety of forms, such as, for example, blends or emulsions, and can be processed by a variety of known techniques. Consequently, a large variety of asphalt based products can be found on the market, and are used in, for example, paving; roofing; joint sealing; specialty paints; electrical laminates; hot melt adhesives, low-grade rubber product dilutents; radioactive waste disposal dilutents; hot-dip coatings; and water retention barriers.

Certain asphalt compounds and similar-type materials, such as, for example, coal tar, bitumen, and substantially non-volatile petroleum based materials (these materials will hereafter be referred to as "base materials") are known generally which flow or are otherwise spread over a surface and which cure to a rubbery, elastomeric consistency due to the presence of a curable prepolymer system. Such compositions, particularly when cold applied, generally require the use of solvents to keep the base material intermixed with the other required components, e.g. elastomeric polymers, prepolymers and/or the like. Examples of such required components

would include isocyanate, styrene-butadiene and/or polybutadiene based elastomers and prepolymers thereof.

To aid in the mixing of the base material with other otherwise non-miscible compounds, organic solvents have generally been used, such as, for example, toluene, aromatic oils, naptha, chlorinated solvents, mineral spirits or carbon disulphide. Such solvents will suspend the base material into a dispersion and allow the other components to intermix with the base material. After mixing, the mixture can be easily applied by conventional technology. Thereafter, the solvent will evaporate off, leaving the asphalt properly intermixed with the other constituents.

However, solvent systems are being criticized by environmentalists and environmental government agencies. Solvents used in curable base material systems are generally deemed harmful to the environment if present above certain levels. Furthermore, persons handling the base material system often risk exposure to these potentially harmful solvents. As a result, government regulations have become increasingly restrictive concerning volatile organic content ("VOC") of base material type coating systems and the like.

Solvents in asphaltic compounds can also cause other problems, such as for example, an undesirable increase in viscosity, particularly at lower temperatures (indeed, many asphaltic systems cannot be applied much below 20°C because of the cell structure present). High viscosity can also make an adhesive difficult to pour, pump or apply.

Yet another problem with solvent based adhesives is the potential for blister formation, particularly when a second coating is placed over the solvent based adhesive. If too little solvent is able to escape, the solvent vapours can accumulate and cause the coating to blister. On the other hand if the solvent is able to escape too freely, the adhesive may "dry up", pull away, or crack due to the rapid loss of solvent.

Furthermore solvents can increase cost due to increased shipping costs, handling costs and the like. Such solvents can also increase the flammability of the substance, and may cause unwanted side reactions.

Moreover, many solvent based systems provide poor green strength, that is, they are not sufficiently tacky (due to the presence of solvent) to provide adequate bonding and/or adhesion immediately upon application and prior to complete or substantial

curing. Without substantial green strength, clamps, supports and the like must be used substantially during the time the material cures.

As a result, a tremendous need exists and has existed for many years for solvent-free base material systems. Substantial research has been done in the industry to find a way to eliminate the need for asphalt solvents. However, for one reason or another, the industry has had to continue using asphalt solvents, much to the consternation of numerous government agencies, environmentalists and other concerned citizens.

It has now been found possible to provide a substantially solvent-free alternative to conventional solvent based adhesives, coatings, sealants and the like.

According to the present invention there is provided a substantially solvent-free composition which comprises a base material dispersed within a liquid prepolymer system, the dispersion being stable at room temperature for at least about 30 days.

The present invention relates to a composition which is an inversion, the base material being suspended within the liquid prepolymer. More particularly, it relates to a compatibilizing agent to

create an inversion between a non-volatile base material and a liquid binder system. The compatibilizing agent is instrumental in causing the base material to be dispersed within the liquid binder system, even where the weight percent of base material is greater than the weight percent of liquid binder.

The binder is a liquid prepolymer system, such as, for example, a polyester or polyether polyurethane liquid prepolymer system, a polyepoxide liquid prepolymer system, or any conventionally known liquid curing system.

The preferred material of the present invention comprises a base material component, a liquid prepolymer ("curable") component, and a non-volatile compatiblizer component. The base material component is used primarily due to its low cost, although such components may also provide advantageous properties, such as, for example, high penetration value and/or waterproof and weather resistance properties. The prepolymer component is primarily present to polymerize within the base material subsequent to application, thereby providing a polymer network within the base material which provides strength and cohesion. The polymer network preferably contains urethane groups or the like which also provide desirable elastomeric properties. The compatiblizer

is used to promote intermixing of the pre-polymer and the base material.

The Base Material Component

The base material component can be any substantially non-volatile organic material, such as, for example, bitumen, asphalt, tar oil, substantially non-volatile petroleum based materials, and the like. The asphalt or bitumen component is most preferred and can be any commercially available bitumen material common to the industry. Preferably, the bitumen is substantially free of water and is substantially free of heterocyclic compounds or compounds which have reactive sites which will react with isocyanates or polyols.

It has also been found that base materials with low softening points, such as less than about 177°C (about 350°F) and preferably about 93°C (about 200°F) or less, generally work better in the present invention than base material with higher softening points. The lower softening points generally provide easier intermixing with the prepolymer when using the compatiblizer used in the present invention than base materials with higher softening points. Furthermore, the elastomeric and sealing properties are often better. However the desired properties of an end-

product are typically dependent upon the end-use of the final product, and therefore depending upon the use, base materials having high softening points may indeed be adequate or perhaps even preferred. The most preferred softening point for any particular application can be determined by ordinary skill and conventional experimentation.

A plasticizer or other non-reactive dilutent is preferably added to the base material to further soften the base material, making it easier to intermix with the prepolymer component. Preferred plasticizers include dibutoxyethyl phthalate ("DBEP"), diisodecyl phthalate ("DIDP"), dibutyl phthalate ("DBP"), butyl benzyl phthalate ("BBP"). dioctyl phthalate ("DOP"), dioctyl sebacate ("DOS"), dioctyl adipate ("DOA"), diethyl butyl sebacate ("DEBS"), dibutoxyethyl glutarate, didecyl glutarate, diisodecyl glutarate, tricresyl phosphate, tributyl phosphate, and still bottom phosphate plasticizers. Phthalic derivative plasticizers are more preferred, and butyl benzyl phthalate is most preferred.

The base material component can sometimes contain reactive sites which will react with the prepolymer components, such as, for example sulphhydryl (-SH), imino ($-NH_2$), substituted amino (-NHR),

carbonamide ($-CONH_2$, substituted carbonamide ($-CONHR$), sulphonamide ($-SO_2NH_2$, substituted sulphonamide ($-SO_2NHR$), thioamide ($-SHNH_2$), and sulphonic ($-SO_2OH$) functional groups. Such reactive sites can be detrimental to the preferred embodiment of the present invention, particularly in a one component version of the present invention (one and two component systems are discussed below in the section entitled "Curing").

Therefore, to prevent unwanted reaction between these reactive sites and the prepolymer component, the asphalt should first be pretreated with a blocking group, such as a reactive isocyanate (such as, for example, a para-toluene-sulphonyl isocyanate or the like), anhydride or carbodiamide. Suitable blocking agents include phthalic anhydride, succinic anhydride, maleic anhydride, calcium oxide or other driers. The anhydride will generally also dispose of any water within the base material, and water has been found generally to also be detrimental to the preferred embodiment of the present invention. The preferred amount of blocking group to be added to the asphalt is about 0.1 to about 5 weight percent, although the optimal amount of the blocking group can depend upon the particular end-use of the material and the type of base material, and therefore the blocking agent may

have to be determined by ordinary skill and experimentation.

The Prepolymer Component

A second component of the preferred embodiment of the present invention is a liquid curable prepolymer, most preferably a polyisocyanate prepolymer system. This preferred polyisocyanate prepolymer is formed from the reaction of an organic polyisocyanate, preferably a diisocyanate, and an organic polyol. The hydroxyl group of the polyol will react with the isocyanate group of the polyisocyanate, and the resulting addition reaction will link the polyol to the polyisocyanate, creating a urethane at the junction of the previously separate molecules. The basic reaction of the diisocyanate with the alcohol is a hydrogen exchange, where the hydrogen of the alcohol attaches itself to the carbon of the isocyanate, and conversely, the hydrogen of the isocyanate becomes attached to the alcohol oxygen, becoming a urethane.

However the isocyanate functional groups are preferably in substantial excess, and therefore, the polyol molecules will add to the polyisocyanate molecules until the polyol molecules are substantially or completely depleted, and the resulting (prepolymer) molecules will have unreacted polyisocyanate

functional groups. The resulting molecules preferably have about 1 to about 10 isocyanate functional groups per molecule.

The prepolymer therefore contains rather large molecules having isocyanate functional groups. The functional groups will be reaction sites during curing. Curing is discussed below under the section heading "Curing".

Virtually any polyisocyanate can be used, including for example methylene di-para-phenylene isocyanate ("MDI"), toluene diisocyanate, polymethylene-polyphenylene-diisocyanate, isophorone diisocyanate, and mixtures thereof. Triisocyanates and higher polyisocyanates also work well. The most preferred polyisocyanates are aromatic polyisocyanates, such as, for example, MDI.

Suitable polyols (for reacting with the polyisocyanate to thereby form the polyisocyanate prepolymer) preferably have urethane or urea forming constituents, such as, for example, polyether polyols and less preferably polyester polyols, including diols and triols such as, for example, glycerine or glycerol. However, acrylated polyols do not work well in the present invention. Suitable polyols include ethylene glycol, propylene glycol, diethylene glycol,

polybutadiene polyols, polytetrahydrofuran polyols, and polycarbonate polyols, and caprolactone-based polyols. Such polyols can be reacted with an alkylene oxide including ethylene oxide, propylene oxide and butylene oxide for example, to form polyether polyol adducts useful in forming the polyisocyanate prepolymer. The polyol can have a weight average molecular weight ranging from as low as about 250 to about 10,000 or more. Less preferred polyols are polyester polyols, since they have been found to be rather water sensitive and somewhat more temperature sensitive.

The polyisocyanate prepolymer also preferably contains one or more non-reactive dilutents, preferably plasticizers. These non-reactive dilutents advantageously modify (typically decrease) the viscosity of the material. The preferred non-reactive dilutents also typically make the end product less temperature sensitive, i.e., more durable when used at temperatures greater than about 66°C (about 150°F). Preferred plasticizers include dibutoxyethyl phthalate ("DBEP"), diisodecyl phthalate ("DIDP"), dibutyl phthalate ("DBP"), butyl benzyl phthalate ("BBP"), dioctyl phthalate ("DOP"), dioctyl sebacate ("DOS"), dioctyl adipate ("DOP") and diethyl butyl sebacate

("DEBS"), dibutoxyethoxyethyl sebacate, dibutoxyethyl sebacate, dibutyl sebacate, dioctyl dodecanedioate, diisooctyl dodecandioate, dioctyl sebacate, dioctyl sebacate (substituted), triisooctyl trimellitate, trioctyl trimellitate, diisooctyl adipate, dioctyl adipate, dioctyl azelate, long chain alkyl alkylether diester, dialkyl diether glutarate, dibutoxyethoxyethyl glutarate, dibutoxyethyl glutarate, tributyl phosphate, still bottom phosphate plasticizers, and aromatic sulphonamides. Phthalic derivative plasticizers are more preferred, and butyl benzyl phthalate is most preferred. The plasticizer softens the prepolymer and the asphalt, making them more fluid and therefore somewhat easier to intermix.

The amount of prepolymer used in the present invention should be adequate to provide a coherent substantially homogeneous mass. Typically this will mean that the prepolymer is present in a weight percentage of about 20 to 90%, preferably about 50%.

The Compactiblizing Agent

The third ingredient of the preferred embodiment of the present invention is a compatiblizer or compatabilizing agent which is defined as any material which will aid in inverting the base material within the liquid prepolymer system, and aid in causing the

base material to be dispersed within the liquid prepolymer stem. The most preferred compatiblizer is a surfactant-type material, having a substantially non-polar portion and a substantially polar-organic portion. The most preferred compatiblizer comprises a polymer unit, or two such units being either identical or different linked together by an ester, carbon or ether bond, said unit having the following formula:

$$CH_3\text{-}(C_nH_{2n})\text{-}R_1$$

wherein:

n is 4 or more, and

R_1 is COOH, COO^-M^+, $COOR_2$ or R_2, preferably $COOR_2$,

wherein:

M is a metal, preferably zinc, and

R_2 is a substantially saturated organic chain having a backbone substantially comprising carbon-carbon, carbon-oxygen, or carbon-nitrogen linkages, or combinations thereof, wherein the backbone's pendant constituents are either -H or -OH and wherein at least one pendant constituent is -OH. The most preferred compatiblizer is obtained where n is 12 or more, and R_1 is $COOR_2$.

The paraffinic portion of the most preferred compatiblizer, $CH_3-(C_nH_{2n})-$, is generally very compatible with the base material. In general, the longer the chain, the more compatible the molecule will be with the base material, and therefore if the chain is relatively short, more compatiblizer molecules will generally be needed to suspend or invert the base material within the liquid prepolymer.

The semi-polar portion of the most preferred compatiblizer polymer, $-R_1$, has been found to be very compatible with polyisocyanate prepolymer, plasticizers and most additives used in asphalt systems which are substantially non-polar, but have polar-organic portions, such as, for example, urethane-type polarity. In the preferred embodiment, the hydroxyl constituent(s) of the semi-polar portion of the polymer is very compatible with the urethane linkage of the prepolymer (or any other organic segment having a polarity substantially similar to urethane).

In the preferred embodiment, the hydroxyl group(s) will tend to move to the urethane linkage(s) and will tend to pull the compatiblizer in relative close proximity to the prepolymer molecule. In addition to the hydroxyl groups, the semi-polar portion of the preferred compatiblizer will also have hydrocarbon

groups which are substantially non-polar and which are very compatible with the non-polar asphalt or bitumen.

As a result, the hydroxyl group will help suspend the urethane or similar type portion of the prepolymer, and the rest of the semi-polar portion of the prepolymer will help suspend the non-polar portion of the prepolmer, while the paraffinic portion of the compatiblizer will generally help suspend the base component. As a result, the compatiblizer lifts the base material and prepolymer into suspension within the prepolymer system, enabling them to be thoroughly and easily intermixed.

Regarding the paraffinic portion of the compatiblizer, the flexibility of the paraffinic chain is important and aids in the ability of the compatibilizer to suspend the base component. Therefore any double or triple bonds or the like would be detrimental to the paraffinic portion.

Furthermore, the non-polar character of the paraffinic chain is also very important. Modifications to the paraffinic chain will generally be detrimental to the compatiblizer, if they make the non-polarity less uniform. In general, even slight deviation from a pure paraffinic chain will generally reduce compatibility.

The semi-polar portion of the compatiblizer however can be varied in a number of ways and is more difficult to define. As with the paraffinic portion, chain flexibility is also important. Chain flexibility aids in the ability of the compatibilizer to suspend both the prepolymer and the base material.

Chain flexibility can be increase by substituting carbon-carbon bonds (in the semi-polar portion) with carbon-oxygen or carbon nitrogen linkages. The increased chain

flexibility increases the ability of the compatibilizer to suspend the base material within the prepolymer, but also effects its polarity. However, the semi-polar portion is designed to have a non-uniform polarity, and it has been found that modication to this non-uniform polarity generally do not substantially diminish compatibility.

The preferred prepolymer generally has numerous urethane linkages, as well as urea linkages and other components having some organic polarity. The polarity of the oxygen and nitrogen portions of the polymer backbone generally are very compatible with these portions of the prepolymer. As a result, although the semi-polar portion may be less able to suspend certain (non-polar) portions of the prepolymer due to the presence of oxygen of nitrogen, the increased chain flexibility enhances compatibility and the polarity due to the oxygen and nitrogen aids in suspending other polar portions of the prepolymer.

The ether or ester linkage between the paraffinic portion and semi-polar portion has generally be found to be advantageous, although a precise explanation for this cannot be given. One explanation might be that the ester provides a stiff link between two very flexible portions of the compatiblizer molecule. Since the two portions are intended to suspend two different components, perhaps the ester aids in keeping the two portions seperate and interactive with their intended component. Perhaps the relatively high polarity of the ester draws the hydroxy portion (and therefore the prepolymer) into close proximity to the paraffinic portion (and therefore the asphalt), thereby allowing improved intermixing. In any event, ester linkages are preferred within the transition zone between the

paraffinic side and semi-polar side but are not preferred as part of either of these two sides. Hence the compatiblizer might be better visualized as having a paraffinic side, a transition portion and a semi-polar side.

Fatty acids are relatively inexpensive and relatively plentiful. Numerous fatty acids were researched, and it was found that they generally provide noteworthy compatibalization (significantly diminish the need for solvent in mixing base material and prepolymer). Metal salts of these fatty acids were also tried, using metals such as, for example, zinc, and the salts also provided noteworthy compatibilization.

The fatty acids were then reacted with alcohols and compatibilization generally increased. Compatibilization was best when a diol or polyol, particularly a diol, was used to thereby provide a paraffinic chain attached by an ester linkage to a flexible chain having one or more hydroxyl groups. Compatibilization was generally better where only one hydroxyl group existed on the chain, preferrably toward the terminal end of the chain.

Fatty acids were reacted with diols, particularly ethylene glycol and propylene glycol. The best compatibilization was achieved when reacting stearic acid and propylene glycol to produce propylene glycol monostearate. The polystearate version of this molecule, bis stearyl ester polypropylene diol, also provided excellent compatibilization.

Further work was therefore done, and it was found that the paraffinic/semi-polar molecule could be linked with another paraffinic/semi-polar molecule (either the same or different) with an ester, ether or carbon linkage, and the resulting molecule would generally work well as a compatiblizer.

However three such molecules linked together generally did not give good compatibilization results in the preferred embodiment.

Polyhydric alcohols were researched, particularly triethylene glycol. Triethylene glycol caprate caprylate and triethylene glycol dipelargonate both provided noteworthy compatibalization, and it is believed that most alcohols reacted with a fatty acid will provide compatibilization, at least to some degree. Polyols with ether groups were reacted with fatty acids and found to also provide exceptional compatibilization.

Variations of the preferred compatibilizer of the present invention may be made, depending upon the end-use and performance requirements of the end-product. For example, the greater the amount of base material to be compatiblized, typically the more important the paraffinic portion of the compatiblizer. Either the paraffinic chain should be very long or a large number of such chains should be present. If a lesser amount of asphalt is used, the optimal compatiblizer may be primarily dependant upon the semi-polar portion of the compatiblizer. If the prepolymer is substantially non-polar, then the semi-polar portion of the compatiblizer should generally be non-polar. If an increased amount of urethane portions are present or if the prepolymer is rather polar, then more hydroxyl groups may be required or more ether linkages to obtain the optimal compatiblizer.

It would be impossible to test and describe all possible variations of the preferred embodiment with respect to

all possible base material-prepolymer systems. The most appropriate compatibilizer will generally depend upon the base material selected. If a base material is used which is more paraffinic-like than asphalt, then the non-polar portion of the compatiblizer should generally be greater. If the base material and/or prepolymer have different combinations of polar organic constituents, then the polar organic portion of the compatiblizer should be modified to accommodate these changes. An important basis for modifying the compatiblizer to accommodate different base materials and/or prepolymer materials is that "likes dissolve likes", that is, the polarities of the constituents of the base material and prepolymer should match (have similar polarity with) segments of the compatiblizer. Preferably one portion of the compatiblizer will have polarity components which match-up with the base material and a second portion having a polarity which matches up with the prepolymer material. Ordinary skill and experimentation may be necessary for determining the appropriate compatiblizer for any particular embodiment of the present invention. Indeed, the compatiblizer need not be a single component. One compatiblizer could be used to provide compatibility directed to the prepolymer, a second compatiblizer could be used to promote compatibility of the base material and yet a third compatibilizer could be used to compatibilize all the constituents into a dispersion. Regardless of how many compatibilizer components are used, the central focus of the present invention is to create a dispersion wherein the base material is dispersed within the liquid prepolymer system.

The compatiblizer preferably is present in the range of about .01% to about 5% with .1% being most preferred (all percentages herein are weight percentages unless otherwise indicated). Since the optimal compatiblizer and compatiblizer concentration may be dependent upon the end-use application of the asphaltic compound, the optimal compatiblizer and compatiblizer concentration can be determined using ordinary skill and routine experimentation.

The compatibilizer used in the present invention substantially diminishes the need for a volatile organic solvent, because the fatty acid derivative (or non-derivative) surprisingly provides sufficient miscibility among the material components to form a flowable, sufficiently intermixed system.

The resulting material can be easily blended or mixed and can be pumped, cast as a film, sprayed or injection molded. The resulting elastomeric material can be useful as a roofing sealer, highway sealer, automotive undercoat, window mastic, or any one of a number of similar-type applications.

The compatiblizer will not interfere with most chemical reactions commonly used in asphalt systems and can be used in a one-part or a two-part system. Unlike traditional organic solvents which can be an environmental and health hazard, the compatibilizer used in the present invention is non-volative and generally relatively non-toxic in comparison to conventionally known solvents or the like.

Curing

The polymerization reaction of the isocyanate prepolymer is commonly referred to as "curing." Prior to curing, the mixture is substantially flowable or moldable, but after

curing, the resulting polymer network will generally cause the material to be a non-flowable, non-moldable elastomeric solid.

Curing creates an adhesive bond to most porous contacting surfaces. The sealant properties of the preferred embodiment typically perform well, because the asphalt component will generally penetrate into the porous surface upon which it is applied, thereby providing the pre-polymer with a substantial contacting surface upon which to bond as it cures.

The curing reaction is generally not reversible, and once the material cures, the material is generally no longer flowable or moldable. If the material is used as a sealant, the resulting elastomeric seal (due to curing) is relatively permanent. If the material is pried away and reapplied to a contacting surface, the material will generally have less desirable sealing properties than it had initially (the base material may again penetrate into the porous surface but the substantial adhesion created due to the curing reaction is generally lost forever).

Not surprisingly therefore, the composition of the present invention is preferably stored and transported in its pre-cured state. The composition is preferably applied and then allowed to cure. Curing can be initiated in a number of ways.

In a one part system, curing is initiated and promulgated by moisture, preferably humidity from the air. As a result, the pre-cured composition is generally transported and stored in a substantially water-free environment. ion is When the composition is applied and exposed to ambient conditions, the water in the air will react with the isocyanate functional groups of the prepolymer, creating an amine (urea) and giving off carbon dioxide as a by-product.

The amine will in turn readily and quickly react with any other isocyanate functional group present. The amine-isocyanate reaction is an addition reaction which links the two prepolymer chains together, creating a disubstituted urea functional group at the connection point of the two prepolymer chains. This curing reaction creates a polymer network within the base material which provides strength, cohesion, adhesion and elastomeric properties.

A plethora of other curing reactions could also be used. A secondary curing agent could be added to the one part system which would also react with moisture to create a reaction product (typically an amine) which would initiate and/or promulgate the prepolymer polymerization. Such secondary curing agents are often found to be useful, because the curing reaction does not produce carbon dioxide as a bi-product which may be advantageous for certain applications. Secondary curing agents for one part isocyanate based polymerization reactions are well known in the art, such as, for example, oxazolidine or ketimine. In a two part system, a curative is mixed into the system just prior to application. In such systems, a large number of acceptable curatives are well known in the industry. Acids, amines, hydroxys, or virtually any hydrogen or proton donating molecule can be used to initiate and promulgate the polymerization of an isocyanate prepolymer.

One part systems are generally preferred however, because end-users typically find that mixing prior to application is unduly burdensome, particularly if certain mixing equipment is necessary or if the length of time and quality of mixing has a small margin for error.

Regardless of whether a one part or two part system is used in the preferred embodiment, a large excess of isocyanate will often also create a cross-linked polymer network, because the urethane or disubstituted urea groups (created at the junction point of two prepolymers) can themselves react with isocyanate to form an allophanate (RNHCOHR'COOR') in the case of a urethane reaction or a substituted biuret (RNHCONR'CONHR") in the case of a disubstituted urea reaction.

Other Additives

Other additives can be added to fine tune the physical properties of the resulting composition. Optional ingredients which can be used include, for example, those catalysts (eg imidizole tin or other known metal catalysts), fillers and additives conventionally used in base materials, driers, stabilizers, isocyanate based polymers, antioxidants, protectants and the like. If the curing reaction gives off carbon dioxide (as when water reacts with an isocyanate functional group), an absorbent can be used, such as, for example, a molecular sieve, to absorb the carbon dioxide, thereby substantially preventing unwanted bubbles or the like which may occur with the evolution of gases during curing.

Preferred fillers would include organoclays. Such filler preferably comprise platelets having long chain organic compounds bonded to their two faces. When used as a filler and when the system is at rest, the long chain components of the organoclay will agglomerate, making the system thick and solid-like. However, when a shearing force is applied, such as, for example, when the material is moved and/or applied, the long chain components will disperse, creating an emulsion which will aid in

the flow properties of the material (the organoclay will no longer thicken the material unless or until it once again comes to a rest and the long chain components once again agglomerate). Such fillers allow for easy application since they do not substantially impede the flow capabilities of the compound while the compound is being applied, and such fillers also thicken the material once it comes to rest, thereby substantially preventing the material from flowing away from the area to which it was applied.

Other possible additives would include those modifiers and additives conventionally used in the formation of natural and synthetic elastomers. Such additives include flame retardants, reinforcements (both particulate and fibrous) heavy and light fillers, UV stabilizers, blowing agents, perfumants, antistats, insecticides, bacteriostats, fugicides, surfactants, and the like. Additionally, it should be recognized that additional conventional elastomers can be included as an ingredient in forming the asphalt material of this invention. Such additional elastomers include for example, polysulphide, EPDM, EPR ethylene, propylene diene monomer, ethylene propylene terpolymer, polychlorobutadiene, styrene-butadiene rubber, butyl rubber, nitrile rubber, and the like.

The Final Product

The resulting material is free of solvent evaporation stress (i.e. cracking, blistering and the like) common to many solvent-based systems. The compatiblizer also surprisingly enhanced the "green strength" of the resulting materials, that is, the ability of the asphalt compound to be tacky and to adhere during the transition period between

the cured and uncured states. The high green strength of the product of the present invention is advantageous, because the composition generally can be used without the need for clamps or similar-type devices since the material will adhere and bond virtually on contact. The adherence and bonding will increase as the curing progresses.

A one step system of manufacture is preferred since it eliminates the need for two-component mixing just prior to application, and the preferred method of manufacturing the one-step system is as follows:

1. The prepolymer is mixed at a slightly elevated temperature 60 to 88°C (140 to 190°F) in a substantially water-free environment and comprises (in weight parts of final material, not weight parts of prepolymer material):

a) about 20 to about 75 weight parts, and most preferably about 34 weight parts of about 2000 equivalent weight polyol;

b) about 2 to about 15 weight parts, and most preferably 7 weight parts non-reactive dilutent, preferably plasticizer;

c) about 2 to about 20 weight parts and most preferably about 7 weight parts of about 150 equivalent weight diisocyanate; and

d) a trace amount of catalyst (preferably tin) preferably at least about 0.01 weight parts.

2. The prepolymer preferably comprises about 20 to about 90 weight parts, preferably about 50 weight parts of the final material. The prepolymer is set aside and not used until step 10 below.

3. The asphalt component is heated in a substantially water free environment to its softening point or until it is substantially a fluid. The amount of asphalt is preferably about 10 to about 80 weight parts, most preferably 28 weight parts. The asphalt should be continually heated to its softening point in a substantially water-free environment throughout the following manufacturing steps.

4. The non-reactive dilutents (most preferably plasticizer(s)) are added to the heated asphalt. The amount of non-reactive dilutents is preferably about 2 to about 28 weight parts, most preferably about 15 weight parts.

5. The blocking agent, preferably an anhydride, isocyanate or carbodiamide, is added. The preferred amount of blocking agent is about 0.2 to about 5 weight parts, most preferably about 0.6 weight parts.

6. The materials are mixed until all materials are dispersed or dissolved.

7. A catalyst is added (preferably tin, imidizole, or other metal catalyst). The preferred amount of catalyst is at least about 0.1 parts per million;

8. Mixing is continued and any desired additives are added (thickeners, thixotropes, antioxidants and protectants). The preferred amount of additives is about 2 to about 25 weight parts.

9. The compatibilizer is then added. The preferred amount of compatiblizer is at least about 0.01 weight parts, most preferably about 0.5 weight parts.

10. The prepolymer is added and the mixing is continued until all materials are dispersed or dissolved.

11. Allow the mixture to cool and store in a substantially water-free environment.

The present invention will now be further described with reference to, but is in no manner limited to, the following Example.

Example

1. The prepolymer was mixed at room temperature in a substantially water-free environment and comprises (in weight parts of final material, not weight parts of prepolymer material):

a) 34 weight parts of a 2000 equivalent weight polyether triol;

b) 7 weight parts butyl benzyl phthalate;

c) 7 weight parts of diphenyl methane diisocyanate; and

d) a trace amount of tin catalyst, about 1

ppm.

2. The prepolymer was set aside in a substantially water-free environment and not used until step 10 below.

3. 28 weight parts of industrial grade asphalt was heated in a substantially water free environment to its softening point. The asphalt was continually heated and mixed at its softening point in a substantially water-free environment throughout the following manufacturing steps.

4. About 14 weight parts of butyl benzyl phthalate was added to the heated asphalt.

5. 0.6 weight parts of maleic anhydride was then added to the heated asphalt.

6. The asphalt mixture was mixed for about 30 minutes until all materials were dispersed or dissolved.

7. A trace amount of tin catalyst was then added, about 0.05 weight parts, and the asphalt was mixed for about 2 hours;

8. 4 weight % of a bentonite clay was then added.

9. 0.5 weight parts of propylene glycol monostearate was then added.

10. The asphalt was mixed until all the materials were dispersed or dissolved and then the prepolymer was added and mixed about 30 minutes until all materials are dispersed or dissolved.

11. The final mixture was allowed to cool and was stored in a substantially water-free environment.

The above mixture was tested and found to properly cure overnight to a commercially acceptable elastomer under most common outdoor weather conditions. The overnight relative humidity can be as low as about 30% and the overnight temperature can be as low as about -18°C (about 0°F) and the material will properly cure in about 10 to about 20 hours. At higher temperatures and relative humidities, the material will cure much more quickly.

The amount of cure time can be adjusted by increasing or decreasing the amount of catalyst in the formulation or by adding an intermediate water curing component in place of the catalyst, such as, for example, oxazolidine or ketimine. The oxazolidine or ketimine can be added in place of the catalyst in an amount of about 0.1 to about 2 weight parts, preferably about 0.5

Upon curing, the resulting product of the Example had excellent peel adhesion, tensile adhesion and lap shear. The material was verydurable and water and weather resistant and would conceivably work very well as a roofing adhesive or the like.

Alternatively, a two-part adhesive can be manufactured wherein the above material is mixed with an amine

or other hydrogen donating compound just prior to application. The amine will react with the prepolymer typically much more readily than will water. As a result, the material will cure much more quickly and will not significantly react with water (and therefore will not significantly give off carbon dioxide as a by-product).

Alternatively, a blocking group can be incorporated onto the isocyanate functional groups so that the material will not react with water. A curative can then be mixed with the material just prior to application which will remove the blocking group and initiate and/or promulgate curing.

The chemistry relating to polymerization of isocyanate prepolymers is well developed and a full discussion of one component and two component curing systems would be so voluminous as to be inappropriate in light of the fact that the present invention is not directed to any particular curing system, but rather to an innovative compatiblizer. Such an exhaustive discussion of curing systems therefore is unnecessary. Such curing systems are readily known or can be readily developed by an ordinary artisan, using routine experimentation and knowledge well known in the art.

CLAIMS

1. A substantially solvent-free composition which comprises a base material dispersed within a liquid prepolymer system, the base material being selected from bitumen, asphalt, coal tar or a substantially non-volatile petroleum based material, and the dispersion being stable at room temperature for at least about 30 days.

2. A composition as claimed in claim 1, in which there is also present a compatiblizing agent.

3. A composition as claimed in claim 2, in which the compatiblizing agent has a non-polar component and a polar organic component.

4. A composition as claimed in claim 3, in which the compatiblizer comprises a polymer unit, or of two such units which are either identical or different and linked together by an ester, carbon or ether bond, said unit having the formula:

$$CH_3-(C_nH_{2n})-R_1$$

wherein:

n is 4 or more, and

R_1 is COOH, COO^-M^+, $COOR_2$ or R_2,

wherein:

M is a metal, and

R_2 is a substantially saturated organic chain having a backbone substantially comprising carbon-carbon, carbon-oxygen, or carbon-nitrogen linkages, or combinations thereof, wherein the backbone's pendant

constituents are either -H or -OH and wherein at least one pendant constituent is -OH.

5. A composition as claimed in claim 4, in which n is 12 or more, and R_1 is $COOR_2$.

6. A composition as claimed in claim 5, in which the compatiblizer is selected from propylene glycol monostearate, bis stearyl ester polypropylene diol, ethylene glycol monostearate, triethylene glycol caprate caprylate triethylene glycol dipelargonate, or combinations thereof.

7. A composition as claimed in any of claims 2 to 6, in which there is at least about 0.01 weight percent compatiblizing agent.

8. A composition as claimed in any of claims 1 to 7, in which the prepolymer is an isocyanate prepolymer.

9. A composition as claimed in any of claims 1 to 8, which comprises

about 15 to about 75 weight percent base material;

at least about 0.01 weight percent compatiblizing agent; and

about 25 to about 75 weight percent prepolymer.

10. A composition as claimed in claim 9, in which the prepolymer comprises:

about 25 to about 65 weight percent polyol,

about 5 to about 20 weight percent plasticizer

and

about 5 to about 20 weight percent diisocyanate.

11. A composition as claimed in any of claims 1 to 10, in which there is also present a blocking agent in an amount of 0.1 to about 5 weight parts.

12. A composition as claimed in claim 11, in which the blocking agent comprises an anhydride, reactive isocyanate or carbodiamide.

13. A substantially solvent-free composition substantially as hereinbefore described with particular reference to the foregoing example.

14. A method of compatiblizing a base material with a liquid prepolymer without the use of solvents, which comprises:

mixing a base material as defined in claim 1 and a prepolymer as defined in claim 1 or 8, with a compatiblizing agent as defined in any of claims 2 to 6.

15. A method as claimed in claim 14, in which the components are used in the amount as defined in any of claims 7, 9 or 10.

16. A method as claimed in claim 14 or 15, in which there is also present a blocking agent as defined in claim 11 or 12.

17. A method of compatiblizing a base material with a liquid prepolymer substantially as hereinbefore described with particular reference to the foregoing example.

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